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(72) Inventors ROLAND EDGAR STAHL and ROBERT KENNETH TUBBS

(19) THE PATENT OFFICE LONDON

(54) WAX AND ETHYLENE/VINYL ESTER COPOLYMER BLENDS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to wax and ethylene/vinyl ester copolymer blends.

The art of extruding wax blends reinforced with polymeric additives such as high molecular weight ethylene/vinyl acetate copolymers is well known; particularly where high performance coatings are desired. To be acceptable, such blends have required a high copolymer concentration and, accordingly, extruded coatings ordinarily display superiority in those properties which are copolymer dependent. Such properties include adhesion, hot tack, flexibility, gloss, and grease resistance. However, due to the high copolymer concentration and the attendant increased cost, extrusion coating has heretofore been limited to only those applications where extraordinarily high performance coatings are required and, consequently, the cost is justified.

On the other hand, it would be desirable if wax blends other than those containing high concentrations of copolymer could be successfully extruded. Such would permit those who presently possess extrusion equipment to supply coatings other than the present high cost, high performance ones. However, heretofore attempts to provide extrudable wax blends with low concentrations of copolymer have by-and-large been unsuccessful. In general, such wax blends have very poor extrudability as evidenced by a large degree of "neck-in" on extrusion. As a consequence of "neck-in", the extruded curtain is thicker at the edges resulting in a coating of non-uniform thickness. Non-uniformity necessitates increased trimming of the coated stock and, accordingly, greater waste.

According to the present invention there are provided compositions which have in our tests shown improved extrusion characteristics compared with compositions containing ordinary copolymers at similar viscosities and copolymer concentrations.

According to the present invention there is provided compositions comprising an extrudable blend of a wax and an ethylene/vinyl ester copolymer which is substantially gel-free (as defined herein), the melt index of the copolymer having been reduced from a higher value to a lower value by treatment with high energy ionizing radiation at a dose rate of at least 1.0 Mrad/min. In view of the improved extrudability of the present blends, they can contain smaller amounts of copolymer and still display acceptable performance.

As stated above, the ethylene/vinyl esters copolymer incorporated into the compositions of the invention are "substantially gel-free", i.e. the copolymers contain less than 10 percent by weight gel. The copolymers are advantageously free from any gel content.

The present blends can additionally contain the various modifying resins frequently employed in wax compositions. Among others, such resins include rosins, rosin esters, derivatives of rosin and rosin esters, polyterpenes, and aromatic copolymers, e.g., alpha methyl styrene/vinyl toluene. When used, the amount of such modifying resin rarely exceeds 30 percent, based on the weight of the blend, and is frequently less than 15 percent. Also, as hereinafter discussed, customary wax reinforcing polymers, e.g., non-irradiated ethylene/vinyl ester copolymers, can also be included in the present blends.

The copolymer melt index is measured according to ASTM D—1238—65T using Condition E (190°C.—2160 grams). Prior to determining the melt index, the copolymers are dusted with 500—1000 ppm of butylated hydroxytoluene (BHT) antioxidant.

The presence of gel in the ethylene/vinyl ester copolymer is determined by measuring the copolymer's solubility in toluene; complete solubility indicating the absence of gel. Solubility in toluene is determined by placing 1 gram of about 1/8" (0.32 cm) copolymer pellets in a 100 mesh stainless steel screen basket suspended in the vapors of refluxing toluene (contained in a 2-gallon vessel containing 2 pints of toluene). If copolymer remains in the basket after exposure for 24 hours, gel is present.

An important characteristic of an acceptable extrusion blend is its ability to be extruded at a high temperature (e.g. above 250°F.) without excessive extrudate "neck-in". High extrusion temperatures are desirable in at least two respects; first, substrate adhesion usually increases as temperature increases, and, secondly, lower coating weights are possible since, due to lower blend viscosity at the higher temperature, higher draw-down rates can be used. In connection with a blend's expected performance at high extrusion temperatures, it has been found that blend melt strength, as hereinafter discussed, is a very important characteristic.

As used herein, melt strength is measured using an apparatus similar to that shown in Figure 1 of the article titled "The Use of Melt Strength in Predicting the Processability of Polyethylene Extrusion Coating Resins" (TAPPI, Vol. 50, No. 1, pp. 20—26). To measure melt strength, a seven-gram sample of the blend is charged into a rheometer cylinder, 0.376" diameter, fitted at the base with a 0.082" diameter capillary. The material in the rheometer is preheated at 95°C. for ten minutes, and then a plunger is inserted into the cylinder. The plunger is attached to a ram mechanism that forces the plunger to travel downward at a speed of 0.059" per minute. The extrudate strand is threaded around the bottom of a free-moving pulley to which is attached a calibrated transducer which feeds a recorder. Thereafter, the strand is wound over another pulley to a variable speed windup device. The apparatus is arranged to allow a continuous monitoring of the take-up speed. The speed is increased gradually until the extrudate strand breaks or maximum speed (260 feet/minute, 1.32 meters/sec.) is reached. Tensions are continuously recorded on the recorder. The melt strength is the tension in grams on the free-moving pulley when the strand breaks.

In order to be acceptably extruded (i.e., low "neck-in") at a high temperature where the above-mentioned benefits concerning adhesion and draw-down rate can begin to be realized, a blend should generally have a melt strength of at least 0.25 grams and, preferably, at least 0.4. While progressively higher melt strengths are desirable, no added advantages result from blends with melt strengths in excess of 4—5.

Heretofore, in order to obtain a wax blend with acceptable extrudability, i.e., a blend having the requisite melt strength, a high concentration, e.g., usually at least 50 percent, of copolymer has been necessary. With respect to the present blends, such high concentrations are not necessary. On the other hand, those of the present blends which do contain upwards of 50 percent copolymer exhibit especially high melt strengths and, thus, can be extruded at temperatures where the advantages relating to adhesion and draw-down rate can be maximized.

Irradiated ethylene/vinyl ester copolymers wherein vinyl acetate is the vinyl ester are preferred for use herein and the invention is discussed with reference thereto. However, ethylene copolymers with other vinyl esters can also be used. Among others, such esters include lower vinyl esters such as vinyl formate, vinyl propionate, and vinyl butyrate, as well as higher vinyl esters such as vinyl palmitate and vinyl stearate. Furthermore, while the present invention is primarily illustrated with binary irradiated ethylene/vinyl ester copolymers, it is also operable with irradiated ethylene/vinyl ester copolymers containing minor amounts, i.e., less than 10 weight percent, of other copolymerizable ingredients such as other vinyl compounds, e.g., vinyl chloride and styrene; other esters, e.g., acrylates and methacrylates; and unsaturated acids, e.g., acrylic and methacrylic acids.

Particularly useful irradiated ethylene/vinyl ester copolymers contain 10—40 weight percent vinyl ester, e.g. vinyl acetate. Copolymers with higher vinyl acetate contents rarely have sufficient compatibility with wax to be suitable. With less than 10 percent vinyl acetate, the copolymer's effectiveness in reinforcing wax diminishes. Preferred copolymers contain about 15—33 weight percent vinyl acetate.

The melt index of the irradiated copolymer is not especially limited so long as it can be blended with wax to form an acceptably extrudable blend, for example a blend having a melt strength of at least 0.25 or, preferably, at least 0.4. As copolymer concentration in wax increases, progressively higher melt index copolymers can be used. At very high, e.g., 70—80 weight percent, polymer concentrations, copolymers with melt indexes of up to 40 can be used. For concentrations of less than 70 percent, copolymers with melt indexes of less than 5 are particularly useful. The present compositions of greatest utility are blends containing 25—65, preferably 33—55, weight percent copolymer. For such compositions, irradiated copolymers having melt indexes of less than 3 and preferably less than 1.5 are most useful. The lower limit on melt index is not critical so long as the copolymer is substantially gel free. Irradiated copolymers with melt indexes as low as 0.01 are thought to be useful. To obtain the desired copolymer melt index, copolymers with different melt indexes can be blended together.

In order to realize the advantages of the present invention, the ethylene/vinyl acetate copolymer is one which has had its initial melt index, i.e., its melt index on direct synthesis, substantially, e.g. greater than 50 percent, reduced by treatment with high energy ionizing radiation. The process of preparing such copolymers is described in our copending application No. (Serial No. 1377207) 53430/71. It was observed that radiation treatment up to a given dose, termed the critical dose, results in a progressive reduction in melt index of ethylene/vinyl acetate copolymers and that the degree of melt index reduction possible without formation of gel is dependent upon the dose rate at which the copolymer is irradiated. At the critical dose, gel begins to be formed. The critical dose for a given copolymer depends on the copolymer's vinyl acetate content (lower as vinyl acetate content increases), degree of hydrolyzable branching (lower as branching increases), and initial melt index (higher as initial melt index increases) as well as whether antioxidant is present during irradiation (higher if such is present). The critical dose is usually less than 10 megarad and copolymers irradiated to the critical dose exhibit more than a 50 percent reduction in melt index. The critical dose for the copolymers of particular interest in the present invention, i.e., those with vinyl acetate contents of 15—33 weight percent and melt indexes of less than 3, is generally less than 3 megarads when the copolymer is irradiated in the presence of an antioxidant.

The rate at which the copolymer is irradiated is particularly important. Surprisingly, it has been found that it is possible to obtain gel-free products of lower melt index by irradiation at high dosage rates than by irradiation at low dose rates in spite of the fact that the total dosage of irradiation is the same. Although this effect is gradual over the entire dose rate range, a dose rate of at least 1.0 Mrad./min. is employed. Preferably, dose rates from 3.0 Mrad./min. should be employed. The higher the dose rate the lower the melt index which can be obtained at the same level of gel content. Accordingly, there is no upper limit on the suitable dose rates for the present invention. The only restrictions result from the limitations of currently available equipment which can produce dose rates up to 3,000 Mrad./min. Preferably, the irradiation process should be carried out at dose rates between 3.0 Mrad./min. and 2,000 Mrad./min.

Any source of high energy ionizing radiation, such as high energy electrons, neutrons, protons, and deuterons as well as x-rays, beta-rays, and gamma-rays is useful in the present process. However, in light of the above-mentioned dose rate effect, it is preferred to choose a source capable of high dose rates (for example, high energy electrons are preferred over Co-60 gamma rays on this basis).

The molecular weight distribution of a copolymer containing 28 weight percent vinyl acetate and having an initial melt index of 4.4 and an MI_p/MI_H ratio of 1.6 irradiated to 0.5 and 0.1 MI was investigated by solvent-nonsolvent (toluene-acetone) extraction fractionation. In both cases the distribution was found to be distinctly bimodal with the high molecular weight peak essentially double the molecular weight of the low molecular weight peak. It is believed that the high molecular weight fraction consists of branched, cross-linked molecules, and it is this fraction which provides the unique properties of the irradiated copolymers.

The choice of wax useful in the extrudable blends of the present invention is not especially limited and can be for example paraffin wax, microcrystalline wax, Fisher-Tropsch wax, polyolefin wax, or mixtures thereof. Ordinarily, the wax is either a paraffin wax or a microcrystalline wax. Paraffin wax is a mixture of solid hydrocarbons derived from the overhead wax distillate fraction obtained from the fractional distillation of petroleum. After purification, the paraffin wax contains hydrocarbons that fall within the formulae $C_{23}H_{48}$—$C_{35}H_{72}$ (generally, C_nH_{2n+2} where n is from 23 to 25). It is substantially colourless, hard, and transluscent material usually having a melting point of 125—165°F. (51—74°C.). Microcrystalline wax is obtained from the non-distillable still residues from the fractional distillation of petroleum. It differs from paraffin wax in having branched hydrocarbons of higher molecular weights. It is considerably more plastic than paraffin wax and usually has a melting point of 150—200°F. (66—93°C.).

Any method by which the wax and copolymer can be intimately blended together can be used to form the present blends. Most conveniently, the wax is melted and heated to a temperature of 250—300°F. (121—149°C.), thereafter, the co-polymer and any other ingredients are added to the wax and the temperature raised to 300—350°F. (149—177°C.) and the mixture agitated to assure uniform polymer dissolution. Subsequently, after solidification, the blend may be pelletized about 1/8"—1/4" (0.32—0.64 cm) uniform pellets to facilitate feeding to the extruder. In order to avoid any possible ingredient decomposition during preparation. it is advisable to admix antioxidant with the wax prior to melting. Ordinarily, the presence of 0.1 weight percent, based on the total blend, of an antioxidant such as BHT (butylated hydroxy toluene) is sufficient.

The blends in Tables 2, 3, and 4 illustrate the present invention. All parts and percentage are by weight unless otherwise indicated. Except for that of the blend, the melt index is determined as previously described. Blend melt index is determined in accordance with ASTM D—1238—65T using Condition A (125°C., 325 grams) and converting the measured flow rate (grams/10 min.) to melt index by the following formula:

$$\text{Melt Index} = \text{Log}^{-1}\ [0.83\ \text{Log (flow rate)} + 1.825]$$

The copolymers were irradiated in the form of about 1/8" (0.32 cm) pellets with high energy electrons using a 2 Mev General Electric resonant transformer at a dose rate of 3.0 Mrad./min. The ratio MI_p/MI_H is the ratio of the melt index of the copolymer, prior to irradiation, to the melt index of the copolymer after substantially complete hydrolysis. This ratio indicates the copolymer's degree of hydrolyzable branching; a ratio in excess of 1 for the Table 1 copolymers being associated with a low amount of branching. Hydrolysis is accomplished in methanol using a sodium methoxide catalyst. After hydrolysis, any remaining base in the copolymer is neutralized with acetic acid and the copolymer dried for 24 hours at 80°C. before the melt index is determined. The copolymers designated by letter in Tables 2, 3, and 4 have the following characteristics:

TABLE 1

	Before Irradiation					
Copolymer	%Vinyl Acetate	Melt Index	MI_p/MI_H	BHT (During Irr.)	Total Dose	Melt Index (After Irr.)
A	28	6	1.6	Yes	.5	2.9
B	28	6	1.6	Yes	1.0	0.7
C	28	6	1.6	Yes	1.2	0.5
D	28	6	1.6	Yes	1.7	0.18
E*	28	3.3	—	—	None	—
F*	28	1.3	—	—	None	—

* Comparative resin.

TABLE 2

Blend*	Copolymer	Parts Copolymer	Paraffin Wax MP 140°F. (60°C.) (Parts)	Melt Strength (Grams)	Blend Melt Index
I	A	50	50	.6	552
II	A	60	40	1.9	170
III	B	50	50	3.2	238
IV	B	40	60	.56	947
V	C	40	60	.73	935
VI	C	50	50**	3.0	180
VII	C	60	40	>10	56
VIII	D	40	60	3.0	470
IX	D	50	50	7.2	110
X	D	60	40	>10	24.7
XI	E	50	50	.22	543
XII	E	60	40	.8	180
XIII	F	50	50	.88	458

* All blends also contain 0.1 weight percent BHT.

** Similar results obtained with paraffin wax, M.P. 154°F. (68°C.)

The advantages of the present invention can be readily appreciated by comparing the melt strength values of the above blends at similar blend melt indexes. The blend with the higher melt strength can be extruded at a higher temperature where adhesion is greater and, due to a lower viscosity, lower coating weights are obtainable. For example, Blend XII (containing unirradiated copolymer E) has a melt strength of 0.8 gram at a melt index of 180. In comparison, Blend VI (containing irradiated copolymer) has a melt strength of 3.0 at the same blend melt index of 180. Thus, Blend VI can be extruded at a higher temperature than can blend XII and, consequently, greater adhesion and lower coating weights can be achieved. Furthermore, there is a cost advantage, since Blend VI contains only 50 percent copolymer whereas Blend XII contains 60 percent copolymer. A similar comparison can be made between Blend XIII (containing unirradiated copolymer F) and Blend VIII (containing irradiated copolymer D). In further comparison, Blends I and II (containing irradiated copolymers) show a significant improvement in melt strength over Blends XI and XII at similar blend melt indexes. This comparison is felt to be quite significant since the melt indexes of the respective copolymers in the blends are close (2.3 for I and II; 2.3 for XI and XII). By comparing Blend XII (containing unirradiated copolymer) with Blend V (containing irradiated copolymer) it is seen that substantially the same melt strength can be obtained with the present blends at a much lower copolymer concentration (40% vs. 60%). Moreover, this comparison points up the fact that the present blends can be extruded at low blend viscosities (high blend melt indexes) and still have acceptable performance. Low viscosity Blend XI (containing an unirradiated copolymer) shows poor extrudability. By comparing Blends II and VI the particularly good advantages of using a highly irradiated copolymer can be seen, i.e., less polymer, higher melt strength at similar blend viscosity.

The actual extrusion performance of the present blends in comparison with blends containing unirradiated copolymers is illustrated by the following Table 3. The extruder employed was a conventional 2.5 inch (6.35 cm) diameter polyethylene extruder (L/D=24/1) made by the Hartig Company.

TABLE 3

Blend	Copolymer	Parts Copolymer	Paraffin Wax MP 140°F. (60°C.) (Parts)	Blend Melt Index	Extrusion Temp.		"Neck-In"			
					°F.	°C.	250 fpm*	500 fpm*	1.25 mps**	2.50 mps**
V	C	40	60	935	236	114	1 9/16″	1 5/8″	3.97 cm	4.13 cm
XI	C	50	50	543	200	93	3″	2 7/8″	7.62 cm	7.3 cm
XVI	E	45	55	1000	200	93	4″	3 3/16″	10.2 cm	8.1 cm

* Speed at which blend is extruded (feet per minute).

** Speed at which blend is extended (moles per second).

Significantly less "neck in" occurs with the blend of the present invention (Blend V) than with either of the comparative blends. Such occurs in spite of the fact that both of the comparative blends contain more copolymer and that Blend XI has a significantly lower melt index. Furthermore, Blend V is extruded at the higher temperature [236°F. (114°C.) vs. 200°F.) (93°C.)] where one would expect more "neck-in".

In addition to having superior extrudability, the present blends possess the good coating properties which ethylene/vinyl acetate copolymer-wax blends are known to have. Accordingly, extruded coatings of the present blends have, among other properties, good resistance to moisture and gas permeation (both flat and creased), good heat sealability, good hot tack, good gloss, good flexibility, and good grease resistance.

Furthermore, as indicated previously, the present blends can contain various modifying resins which are useful in improving one or more of the above-mentioned properties. Table 4 illustrates useful blends containing such resins.

TABLE 4

Blend*	Copolymer	Parts Copolymer	Paraffin Wax MP 140°F. (60°C.) (Parts)	Modifying Resin (Parts)	Melt Strength (Grams)	Blend Melt Index
XIV	B	40	50	10(a)	.70	739
XV	C	40	50	10(b)	.60	—
XVI	C	40	50	10(c)	.82	—
XVII	C	40	40	20(d)	.80	549
XVIII	C	40	50	10(c)	.64	—
XIX	C	40	50	10(a)	.70	—
XX	C	40	50**	10(a)	.60	745
XXI	C	40	50	10(d)	.50	827
XXII	C	40	50**	10(d)	.62	743
XXIII	C	40	30	30(d)	1.5	353
XXIV	D	30	60	10(c)	.46	2044
XXV	D	30	60	10(b)	.44	2186
XXVI	D	30	60	10(d)	.40	2057

*All blends also contain 0.1 weight percent BHT.
**Includes 10 parts "Microwax" MP 177°F. (80.5°C.)
(a) "Foral" 85 (esterified wood rosin).
(b) "Piccolyte" α-125 HM (polyterpene).
(c) "Piccotex" 75 (vinyl toluene copolymer, softening point, 75°C.)
(d) "Foral" 105 (thermoplastic ester resin derived from pentaerythritol, softening point, 102—110°C.
(e) "Stabelyte" Ester 5 (thermoplastic resin prepared from glycerine and hydrogenated rosin, softening point, 79—86°C., Acid No., 3—6).

"Foral" and "Piccolyte" are Trade Marks.

In general, the above-discussed modifying resins replace a portion of the wax in the present extrudable blends. However, the present blends also include compositions wherein a portion of the irradiated ethylene/vinyl ester copolymer is replaced by an additional polymer which is compatible with wax and functions as a wax reinforcing resin. While the basic melt strength and enhanced extrudability of the blend is still derived from the remaining amount of irradiated copolymer, the presence of the replacement polymer frequently contributes to end-use properties such as adhesion, hot tack and grease resistance. Also, there may be economic advantages in replacing a portion of the irradiated copolymer. Ordinarily, replacement of the irradiated copolymer only occurs when the irradiated copolymer has a low melt index, e.g., less than 1.5 and, preferably, less than 0.5.

While a variety of wax compatible, wax reinforcing polymers can be used as replacement polymers, the most commonly employed are ethylene copolymers containing at least 60, and usually at least 67, weight percent ethylene. The following are useful: non-irradiated ethylene/vinyl ester copolymers (e.g. ethylene/vinyl acetate); ethylene/vinyl ester/carboxylic acid copolymers (e.g., ethylene/vinyl acetate/acrylic acid or methacrylic acid); ethylene/carboxylic acid copolymers (e.g., ethylene/acrylic acid or methacrylic acid); ethylene/acrylate or methacrylate copolymers; ethylene/carbon monoxide copolymers; ethylene/sulfur dioxide copolymers; and ethylene/vinyl alcohol copolymers.

The replacement polymer should not be used in an amount which prevents the extrusion advantages of the present invention from being realized. While, for all cases, the replacement resin should preferably not be used in an amount which reduces the melt strength of the blend to below 0.25, preferably not below 0.4, the particularly appropriate amount for a given blend will depend on a number of factors such as the character, e.g., melt index and degree of branching of the irradiated copolymer, the character of the replacement polymer, and the desired temperature of extrusion. The appropriate amount of replacement resin for a given end-use application can be determined easily by simple experimentation. For example, initially the total amount of polymer in a blend should be established. Thereafter, a blend should be made up with the total polymer content being irradiated copolymer and the melt strength determined. This will give a rough indication of the extent to which the irradiated copolymer can be replaced. Thus, if the melt strength of the binary blend is close to 0.4, very little replacement would be possible. On the other hand, if the melt strength of the blend is high, e.g., 1—4, considerable replacement can be made. Subsequent to determining the melt strength of the binary blend, blends containing increasing amounts of replacement polymer can be formulated and tested until the appropriate blend is obtained.

Table 5 illustrates the use of replacement resins in wax blends containing the aforementioned copolymer D. The replacement resins are reasonably linear (e.g., MI_p/MI_H about 1.5) ethylene/vinyl acetate copolymers with the indicated melt indexes. Blends containing the maximum percentage of replacement resin have a melt strength of about 0.25.

TABLE 5

Weight Percent* Total Polymer (Copolymer D Plus Replacement Copolymer)	Maximum Replaceable Weight Percent of Copolymer D			
	Melt Index of Replacement Copolymer			
	2.2 MI	6 MI	15 MI	42 MI
30	40	35—40	35	—
40	85	80	70	70
50	—	95	90	85

* On the basis of the whole composition.

If, instead of copolymer D, copolymer C were the basic irradiated resin, the maximum replaceable amount would be less than indicated in Table 5 since copolymer C has a higher melt index than does copolymer D. Similarly, if the melt index of the basic irradiated copolymer were lower than that of copolymer D, greater amounts of replacement resin than indicated in Table 5 could be used. With respect to the amounts set forth in Table 5, it should be emphasized that these represent maximum amounts. Ordinarily, the amount of irradiated resin which is replaced by a non-irradiated ethylene copolymer is considerably less than the maximum permissible quantity. To be assured of acceptable performance, the replacement copolymer should preferably have a melt index of less than 10, preferably less than 7, and it should preferably only replace up to 50 percent by weight, and move preferably only up to 25 percent by weight, of the irradiated copolymer.

WHAT WE CLAIM IS:—

1. Compositions comprising an extrudable blend of a wax and an ethylene/vinyl ester copolymer which is substantially gel-free (as defined herein), the melt index of the copolymer having been reduced from a higher value to a lower value by treatment with high energy ionizing radiation at a dose rate of at least 1.0 Mrad./min.

2. Compositions as claimed in claim 1 wherein the blend has a melt strength of at least 0.25 at 95°C.

3. Compositions as claimed in claim 2 wherein the copolymer contains 10—40 weight percent vinyl ester.

4. Compositions as claimed in any one of the preceding claims wherein the blend has a melt strength of at least 0.4 at 95°C.

5. Compositions as claimed in any one of the preceding claims wherein the vinyl ester comprises vinyl acetate.

6. Compositions as claimed in any one of claims 1 to 4 wherein the vinyl ester comprises vinyl formate, vinyl propionate, vinyl butyrate, vinyl palmitate or vinyl stearate.

7. Compositions as claimed in claim 5 wherein the copolymer contains from 15 to 33 weight percent of copolymerized vinyl acetate.

8. Compositions as claimed in any one of the preceding claims wherein the copolymer contains less than 10 weight percent of a further copolymerized monomer.

9. Compositions as claimed in claim 8 wherein the further copolymerized monomer comprises a vinyl compound, or an unsaturated carboxylic acid or ester thereof.

10. Compositions as claimed in claim 9 wherein the said monomer comprises vinyl chloride, styrene, or acrylic or methacrylic acid or an ester thereof.

11. Compositions as claimed in any of the preceding claims wherein the blend contains up to 80 weight percent of the copolymer.

12. Compositions as claimed in claim 11 wherein the blend contains from 25 to 65 weight percent of the copolymer.

13. Compositions as claimed in claim 12 wherein the blend contains from 35 to 55 weight percent of the copolymer.

14. Compositions as claimed in claim 12 or claim 13 wherein the melt index of the irradiated copolymer is less than 3.

15. Compositions as claimed in claim 14 wherein the melt index is less than 1.5.

16. Compositions as claimed in any one of the preceding claims wherein the reductions of the melt index of the copolymer was accomplished at a dose rate of from 3.0 to 2000 Mrad./min.

17. Compositions as claimed in any one of the preceding claims wherein the wax comprises paraffin wax, microcrystalline wax, Fisher-Tropsch wax, polyolefin wax or a mixture of two or more thereof.

18. Compositions as claimed in claim 17 wherein the wax comprises a hydrocarbon wax of formula C_nH_{2n+2} wherein n is an integer from 23 to 35.

19. Compositions as claimed in claim 18 wherein the hydrocarbon wax has a melting point of from 125° to 165°F.

20. Compositions as claimed in claim 17 wherein the wax comprises microcrystalline wax having a melting point of from 150° to 200°F.

21. Compositions as claimed in any one of the preceding claims wherein a part of the copolymer is replaced by a wax compatible, wax reinforcing polymer.

22. Compositions as claimed in claim 21 wherein the reinforcing polymer contains at least 60 weight percent of copolymerized ethylene.

23. Compositions as claimed in claim 22 wherein the reinforcing polymer contains at least 67 percent of copolymerized ethylene.

24. Compositions as claimed in any of claims 21 to 23 wherein the reinforcing polymer comprises a non-irradiated ethylene/vinyl ester copolymer, an ethylene/vinyl ester/carboxylic acid copolymer, an ethylene/carboxylic acid copolymer, an ethylene/acrylate or methacrylate copolymer, an ethylene/carbon monoxide copolymer, an ethylene/sulfur dioxide copolymer or an ethylene/vinyl alcohol copolymer.

25. Compositions as claimed in claim 24 wherein the reinforcing polymer comprises an ethylene/vinyl acetate copolymer or an ethylene/vinyl acetate/acrylic or methacrylic acid copolymer.

26. Compositions as claimed in any of claims 21 to 25 wherein the reinforcing polymer has a melt index of less than 10.

27. Compositions as claimed in claim 26 wherein the reinforcing polymer has a melt index of less than 7.

28. Compositions as claimed in any of claims 21 to 27 wherein not more than 50 percent by weight of the copolymer is replaced by reinforcing polymer.

29. Compositions as claimed in claim 28 wherein not more than 25 percent by weight of the copolymer is replaced by reinforcing polymer.

30. Compositions as claimed in any one of the preceding claims wherein the blend is one which has been prepared by first melting the wax and then mixing the copolymer and, when used, the reinforcing polymer therewith.

31. Compositions as claimed in claim 30 wherein the blend is one wherein an antioxidant has been admixed with the wax prior to melting.

32. Compositions as claimed in any one of the preceding claims in the form of pellets.

33. Compositions as claimed in any one of the preceding claims wherein a modifying resin is present in an amount of up to 30% by weight of the composition.

34. Compositions as claimed in any one of the preceding claims wherein the copolymer is one whose melt index has been reduced by more than 50% by irradiation.

35. Compositions as claimed in any one of the preceding claims wherein the copolymer is gel-free.

36. Compositions as claimed in claim 1 substantially as herein described.

37. Compositions as claimed in claim 1 substantially as herein described in any of the Examples.

For the Applicants,
FRANK B. DEHN & CO.,
Chartered Patent Agents,
Imperial House,
15—19, Kingsway, London, WC2B 6UZ.

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